THE FORMATION AND DECOMPOSITION OF DITHIONATES

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DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

JACOB CORNOG

The Ohio State University
1921

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I. THE POLYTHIONATES

Dithionic acid, $H_2S_2O_6$, the first member of this remarkable group of acids, was discovered in 1918 by Welter and Gay-Lussac[1]; trithionic acid, $H_2S_3O_6$, in 1842, by Langlois[2]; tetrathionic acid, $H_2S_4O_6$, in 1843, by Fordos and Gelis[3]; pentathionic acid, $H_2S_5O_6$, in 1845, by Wackenroder[4]; finally potassium hexathionate, $K_2S_2O_6$, was discovered in 1888 by Debus[5] as a part of his classic investigation of Wackenroder's solution. Dithionic acid was originally called hyposulfuric acid (*unterschwefelsauer* in the German). The present nomenclature was suggested by Fordos and Gelis[6] in 1847 to simplify the naming of the increasing number of polythionic acids which were being discovered about that time. However the name hyposulfuric persists occasionally as late as 1880.

The obviously outstanding feature of these acids is the "piling up" of sulfur atoms in the molecule, increasing in number one atom at a time, from dithionic acid with two to potassium hexathionate with six sulfur atoms to the molecule. This is a promising field for investigation of valence and molecular structure. Indeed the molecular structure of the polythionates has already been the aim of much investigation, but apparently, thus far, results are more speculative than real. Without attempting a complete discussion of the results already attained in this field, the following facts and observations are mentioned.

Debus[5] experimentally found that all the polythionates, save dithionate, are intermediate products between hydrogen sulfide and sulfur dioxide, on the one hand, and free sulfur and water on the other, as represented by the equation

$$2\ H_2S + SO_2 = 2H_2O + 3\ S.$$

The sulfur in the sulfur dioxide represents a higher state of oxidation than does the sulfur in any of the polythionates save the dithionate. So apparently the whole series of polythionates occurring between the first and last products of the above equation represents a "running down process" in the degree of oxidation of the sulfur. This opinion is in harmony with the findings of Thomsen[7] in the matter of heats of formation. He found for

the whole series of polythionates, that the heats of formation vary uniformly and inversely as the number of sulfur atoms in the respective molecules. From the decreasing heats of formation with increasing number of sulfur atoms in the molecule it would seem that there is an upper limit to the number of sulfur atoms that may occur in a single molecule, and further that the processes of formation and decomposition are not spontaneously reversible.

A further characteristic action of the polythionates occurs on their spontaneous decomposition in water solution under the influence of heat. Although in none of them is the sulfur found in a state of oxidation corresponding to that of sulfates, yet all of them on spontaneous decomposition in water solution yield sulfates as one of the chief products, along with sulfur dioxide and in some cases sulfur. This phenomenon in which a polythionate breaks down into products representing both a higher and a lower state of oxidation of the sulfur than is found in the parent substance is alluded to in the present work as "autoxidation". Such in brief, in the opinion of the author, are one or two of the more salient aspects of the general subject of polythionates. Since the formation of one or more of the polythionates is a very frequent factor in actions involving sulfur dioxide and in view of the wide importance of sulfur dioxide, it was thought desirable on the part of this laboratory to attempt a series of studies of this very interesting and important family of compounds in the hope of amplifying present knowledge of the subject and perhaps ultimately formulating a rational theory of molecular structure. In pursuit of this aim the following studies have been completed.

The Action of Sulfurous Acid on the Sulfides of Iron, Zinc, and Manganese.

Henderson and Weiser. Journal of the American Chemical Society. *35*, 239.

Preparation and Decomposition of Some Thiosulfates.

Henderson and Hummel. (In Preparation.)

Preparation and Decomposition of Tetrathionates.

Henderson and Scott. (In Preparation.)

The present work contemplates a study of "the dithionates along lines indicated in the title. It is hoped that other papers will be forthcoming.

II. A REVIEW OF THE LITERATURE PERTINENT TO THE FORMATION AND DECOMPOSITION OF DITHIONATES.

A survey of the literature shows that the preparation, analysis, crystallography, and determination of chemical and physical properties have been rather thoroughly though by no means exhaustively studies. Salts of nearly all the common and many of the rare metals have been prepared. Many double salts are known though, singularly, no acid salts have been observed. In the resume of the literature which follows, there are included, as being pertinent to the present work, only those citations which bear on the formation or decomposition of dithionates. An extensive bibliography covering the entire field of dithionates is to be found in the files of the Chemistry Department of Ohio State University. The reason for this exclusion is that the bibliography is large and much of it without significance in the present work. Reference works such as Gmelin-Kraut or Abegg's "Handbuch" or Hoffman's "Lexikon" contain rather complete records of papers published on dithionic acid and its various salts.

The partly accidental discovery of dithionic acid was recorded by Welter and Gay-Lussac[1] as occurring in the following manner. M. Welter, a manufacturer of bleach, in attempting to recover the manganese dioxide that had been used in making chlorine, treated the spent material with sulfur dioxide. As a result he obtained a "neutral bisulfite" which he believed "to be at the base of manganese dioxide." At this point Welter consulted Gay-Lussac, with the ultimate result that dithionic acid and the manganese, barium, calcium, strontium, and potassium salts were prepared and described. The mode of preparation, more fully discussed later, was by the passage of a stream of sulfur dioxide through a water suspension of manganese dioxide, whereby manganese dithionate, along with manganese sulfate, was formed. Barium dithionate was prepared by double decomposition between barium hydroxide and manganese dithionate. Dithionic acid was prepared by treating barium dithionate with an equivalent of sulfuric acid. After removal of the resulting barium sulfate by filtration, the remaining water solution of dithionic acid was concentrated by evaporation under reduced pressure to a density of 1.375. Attempts at further concentration resulted in the decomposition of dithionic acid into sulfuric acid and sulfur dioxide.

In 1826, Heeren[8] published the results of a rather extensive work on dithionates. He found that high yields of manganese dithionate were promoted by the fineness of the manganese dioxide used in the suspension, the purity of the manganese dioxide used, and by the maintenance of a low temperature during the time in which the action occurred. Heeren prepared some twenty salts, giving much attention to crystalline structure. He observed that dithionic acid and many of its salts in water solution spontaneously decompose into sulfur dioxide and the corresponding sulfate.

Jacquelain[9] learned that a water solution of sulfur dioxide in a tightly stoppered bottle after standing two years at room temperature contained sulfurous, sulfuric, and dithionic acids. Pean de Saint Gilles[10] found that dithionates in small quantities were formed by the action of permanganate on sulfur dioxide, also that dithionates are not oxidized by permanganate. Hauer[11] prepared sodium dithionate by neutralizing a solution of sulfurous acid with sodium carbonate. After this the solution was heated with finely divided manganese dioxide. When the excess manganese dioxide had been removed, crystals of sodium dithionate were obtained by concentrating the solution. Gelis[12] first completely described the action of sulfur dioxide on ferric hydroxide as a general method for preparation of dithionates. This is one of the best methods for preparation on a laboratory scale. Rathke and Zschiesche[13] prepared sodium dithionate according to the equation $2Na_2SO_3 + Se = Na_2Se + Na_2S_2O_6$. Sokolow and Multschewski[14] show that under proper conditions the following action occurs. $2NaHSO_3 + I_2 = 2NaI + H_2S_2O_6$.

Kluss[15] studied the salts of metals having more than one valence and of metals just above and below hydrogen in the electrochemical series. Except in the matter of the composition of the salts prepared he records no experimental data. As bearing on the present work it may be gathered from the work of Kluss that:

1. Heating solutions of dithionic salts, except those of the alkali and alkaline earth metals, causes spontaneous decomposition into sulfur dioxide and the corresponding sulfate.

2. The temperature at which decomposition begins varies in a general way with the position of the metal in the electrochemical series, *i. e.* the higher the position in the series the higher the temperature at which decomposition occurs.

3. Dithionates of the alkali and alkaline earth metals can be boiled in saturated solutions without decomposition.

4. Of metals having more than one valence, the "ous" salt decomposes as already outlined, while the "ic" salt decomposes with the formation of both "ous" and "ic" sulfates along with liberation of sulfur dioxide, and where possible a basic salt may be formed. The sequence of these actions is not to be deduced from the article.

Berthelot[16] found that bromine water decomposes all the polythionates into sulfates. Antony and Lucchesi[17] found that ruthenium dithionate is formed when sulfur dioxide is led through a solution of ruthenium sulfate. They say that the resulting ruthenium dithionate is decomposed by potassium permanganate into sulfate. No other workers have observed the decomposition of dithionates by this reagent. Nabl[18] obtained barium dithionate in small quantity by treating barium sulfite with sulfur dioxide.

The careful work of Carpenter[19] shows that cobaltic hydroxide as well as manganic and ferric hydroxides can be used with sulfur dioxide to form dithionates. He prepared ferrous dithionate in quantities as required by the equation

$$2Fe(OH)_3 + 3SO_2 = FeS_2O_6 + 3H_2O + FeSO_3,$$

obtaining 96% of theoretical yield along with a small quantity of sulfate. With manganic hydroxide he obtained 75% and with cobaltic hydroxide 35% of theoretical yield as required by equations corresponding to the one just set forth for iron hydroxide. The sulfur not found in the dithionate was recovered as sulfate. No dithionate was obtained with a similar action between nickelic hydroxide and sulfur dioxide. Carpenter points out that the yields of dithionate with these metallic hydroxides varies directly as the heat absorbed in their reduction from the "ic" to "ous" hydroxide. For this reduction ferric hydroxide absorbs 546 calories, manganic hydroxide 448 calories, cobaltic hydroxide 225 calories, while nickelic hydroxide *gives off* 13 calories in this process.

Foerster and Friessner[20] and Friessner[21] prepared sodium dithionate by the electrolysis of sodium sulfite. Baubigny[22] describes the formation of dithionates by boiling silver sodium sulfite and the same author[23] prepared dithionate by the action of sodium sulfite on copper sulfate.

Numerous theories have been advanced during the past century seeking to explain the mechanics of the action of sulfur dioxide on manganese dioxide to form both dithionate and sulfate concurrently. Only a few of the more recent ones are mentioned. J. Meyer[25], from an investigation somewhat similar to that of Carpenter, formulated a theory that required that a molecule of sulfate be formed for each molecule of dithionate. Marino[26] demonstrated that the proportion of sulfate to dithionate varies with temperature, thus rendering the theory of J. Meyer untenable. Marino thinks the chief reaction is $MnO_2 + 2SO_2 = MnS_2O_6$ and that the sulfates always found are to be accounted for by the secondary action $MnS_2O_6 + MnO_2 = 2MnSO_4$. In Abegg's "Handbuch"[27], the chemical induction theory of Luther and Schilow[28] and Schilow[29] is applied to the action in question. The "chemical induction" theory supposes that two substances *A* (the actor) and *B* (the acceptor), which under ordinary conditions reacts very slowly, may be caused to react rapidly when a third substance *C* (the inductor), which reacts readily with *A*, is placed in the system along with *A* and *B*. That is, the actor *A* and the acceptor *B*, which ordinarily do not react, may be caused to react by the presence of the inductor *C*, which itself readily and simultaneously acts on *A*. Abegg points out that this theory fits the case of manganese dioxide and sulfur dioxide very nicely. "The actor is the oxidizing agent manganese dioxide, the inductor is sulfur dioxide, and the acceptor the manganese dithionate." The increasing amounts of manganese sulfate formed with rising temperature are explained by saying that heat accelerates the induced action. While the foregoing theory is in harmony with experimental facts, yet it seems to the author that a simpler explanation, which fits the facts equally well, may be formulated. Such an explanation will be attempted later when the experimental facts of the present work have been set forth.

III. SCOPE AND AIMS OF THE PRESENT WORK

The general aim of this work is to attempt a contribution to existing knowledge of polythionates, as a part of the general program of studies in this field being conducted in this laboratory. The specific aim is to study the formation and decomposition of the dithionates with the hope that such knowledge may lead to fuller understanding of their molecular structure and

chemical behavior. As the formation of dithionates has already received considerable experimental attention, the result of which is available, little attention is given to formation in the experimental part of this work. On the other hand, while one frequently reads that dithionates in water solution decompose into sulfur dioxide and the corresponding sulfate, yet a search of the literature fails to reveal a single quantitative study of this matter. Indeed even qualitatively no greater substantiation is generally offered than the bare statement of fact. Concerning the alkali and alkaline earth dithionates Kluss[15] records that their saturated solutions are not decomposed on boiling, while Abegg under barium dithionate says that this substance is decomposed at 155° into the sulfate and sulfur dioxide, giving a citation to Deregibus as authority for the statement. The citation to Deregibus is incorrectly recorded by Abegg and could not be obtained from other sources. In view of the foregoing, it is the purpose of the experimental part of this study to attempt a quantitative study of the decomposition in water solution of a few of the characteristic dithionic salts, particularly those of the alkali and alkaline earth metals. The ultimate aim is the formulation of a reasonable theory of the course of the decomposition. The decomposition of barium dithionate was first and most extensively studied. All salts subsequently studied were found to decompose substantially as barium dithionate. Only minor differences were noted; these are specifically mentioned with the work on individual salts.

Since, at the present time, dithionic salts are not obtainable from commercial sources, it was necessary to prepare all salts used. Barium dithionate is the parent substance from which all other dithionates are usually made, so mention is here made of the work done in its preparation.

IV. PREPARATION OF BARIUM DITHIONATE

Two methods of preparation of barium dithionate were used, the original method of Welter and Gay-Lussac[1] and the method of Gelis[12]. Only a brief outline is here recorded of the processes, which though somewhat long and tedious are not particularly difficult. A fuller description may be found in the literature already mentioned. The quantities of materials mentioned are about as large as can be conveniently manipulated with ordinary laboratory apparatus.

1. METHOD OF WELTER AND GAY-LUSSAC [1]

Preparation of Manganese Dioxide Suspension.

90 to 100 grams of potassium permanganate is dissolved in about 500 cc. of water contained in a two-liter Erlenmeyer flask. The solution is heated to boiling and a quantity of methyl alcohol sufficient completely to reduce the permanganate to a more or less hydrated manganese dioxide is slowly added. The action is vigorous; no trace of pink color remains in the supernatant liquor when reduction is complete. The physical condition of the precipitate varies considerably from time to time. In freeing the precipitate from impurities filtration by suction is undesirable because of difficulty in again getting the precipitate in a suspended condition. Washing by decantation when the precipitate settles readily is satisfactory. Ordinarily the precipitate does not settle readily; resort may be had to the expedient of diluting the suspension to the capacity of a large beaker and then separating the solid and liquid portions by filtration through filter paper on an ordinary funnel. Repeating the process six to ten times is usually sufficient.

The manganese dioxide suspension thus prepared is slowly added to a well cooled saturated solution of sulfur dioxide, through which a stream of sulfur dioxide is slowly passed. The action is rapid and is accompanied by considerable evolution of heat. The solution is kept near 0°, air is excluded and a good excess of sulfur dioxide is maintained until solution is complete. In practice it was found to make no practicable difference in the final yield whether the above procedure was observed or the suspension was first placed in the flask and kept cool while sulfur dioxide was bubbled through until solution was complete.

When the suspension is completely dissolved there is present in the solution sulfur dioxide, manganese sulfate and manganese dithionate. The addition of a concentrated barium hydroxide solution precipitates everything but the dithionate, all dithionic salts being water-soluble. The manganese dithionate is converted into barium dithionate by the barium hydroxide. After filtration the excess barium hydroxide is precipitated by carbon dioxide. When the barium carbonate thus formed has been removed by filtration the solution is boiled to remove any barium bicarbonate which may be present. When this has been removed the solution remaining is concentrated to a density of

about 1.24 to 1.25 and crystals are allowed to form. The concentration of the original barium dithionate solution may be accelerated by boiling while very dilute, but concentration at 50° to 60° until crystals just begin to form on the bottom of the vessel is a safer procedure. If at this point the crusts which generally form are "washed down" with a minimum quantity of hot water and the solution is then allowed to cool overnight a good yield of well formed first-crop crystals is obtained. Yield, 15 to 25 grams.

Although, theoretically, a saturated solution of barium dithionate is not affected by temperatures up to 100°, yet in practice it frequently happens that an appreciable quantity of a very finely divided white powder, probably barium sulfate, is formed when concentrated solutions of barium dithionate are boiled or filtered under reduced pressure during the process of preparation. This may be partly accounted for by remembering that barium sulfate has an appreciable though slight solubility. When the solution is much reduced in volume precipitation results. However, there is a high degree of probability that concentrated barium dithionate solutions slightly decompose at temperatures below 100°. It was found in the present work that apparently over a considerable range of temperature decomposition does not occur consistently. There is evidently some factor operating with which we are not acquainted.

The barium sulfate formed during concentration of barium dithionate is usually too fine to be removed by filter paper. It may be removed by diluting the solution to less than saturation at room temperature and allowing it to stand twenty-four hours, when all solids will settle to the bottom. It may be further observed that in water solution, first-crop barium dithionate crystals yield a light straw-yellow solution. After two or three recrystallizations of the barium dithionate the solution is entirely transparent and colorless.

2. METHOD OF GELIS

The ferric hydroxide suspension may be prepared by dissolving 125 grams of ferric sulfate in a liter of water and adding sufficient sodium carbonate to cause complete precipitation as ferric hydroxide. The ferric hydroxide may be purified in a manner similar to that described for manganese dioxide. The

reaction between ferric hydroxide and sulfur dioxide in its general aspects is similar to that described for manganese dioxide and sulfur dioxide. However, the reaction for ferric hydroxide is not instantaneous, but is a matter of hours and days. This process has the advantages of using cheaper materials, giving better yields, and being successfully conducted at room temperatures without the use of artificial cooling. The following manipulation to bring about action between ferric hydroxide and sulfur dioxide has been employed with satisfaction. The ferric hydroxide suspension is placed in a large Erlenmeyer flask provided with a motor-driven stirring device. The air is excluded as much as possible, while the sulfur dioxide is slowly bubbled through the suspension. The stirring and passage of sulfur dioxide may be discontinued overnight or for a few days at a time with apparently no detrimental results. The stirring and passage of sulfur dioxide are maintained continuously or intermittently until the solution of ferric hydroxide is approximately complete. Following the solution of the ferric hydroxide the procedure is the same as that already described under the method of Welter and Gay-Lussac, except of course one must test for the complete removal of iron and not manganese after the barium hydroxide precipitation. Usual yield 25 to 40 grams.

3. PREPARATION OF DITHIONIC ACID AND DITHIONIC SALTS FROM BARIUM DITHIONATE

With barium dithionate as a mother substance dithionic acid and the dithionic salts of metals having soluble sulfates are readily obtained by treating sulfuric acid or the sulfate with an equivalent of barium dithionate. Dithionic salts of metals having insoluble sulfates may be prepared by treating dithionic acid with an excess of the metallic carbonate, oxide, or hydroxide.

V. DECOMPOSITION OF VARIOUS DITHIONATES. (EXPERIMENTAL.)

1. GENERAL CONSIDERATIONS AND PROCEDURE

As a first approach to the experimental study of decomposition it was necessary to learn how decomposition could be insured, whether it was complete or incomplete, and if incomplete whether there existed a quantitative relation between the products of decomposition that would allow the formulation of a

reasonable theory of the mechanics of decomposition. In the earlier stages many results were apparently indeterminate and inharmonious. In none of the salts studied was complete decomposition secured at 100°. Some salts required about 180° to insure complete decomposition. Working at temperatures above 100° necessitated working in closed systems under pressure. Considerable time was lost finding glass containers that were sufficiently insoluble in water at 180° to prevent vitiation of results from dissolved glass. Pyrex glass and Jena combustion tubing were the most resistant of glasses tried. Sealed tubes as well as pressure bottles of various types were tried. Under the conditions of the experiments the glass in most commercially obtained pressure bottles was so soluble as to make them worthless. Bottles in which "citrate of magnesia" is usually sold at drug stores were usually good for two or three heatings. A new type of pressure bottle was developed and found satisfactory under conditions used. The glass part was a straight-sided cylinder of heavy pyrex glass, sealed off and flattened at the bottom and "flared" at the top. The top was ground down so as to make a tight joint with a plate of thick glass, which was used as a cover. More conveniently, where it will not interfere with results, a rubber gasket may be inserted between cover and pressure bottle. For making gaskets that would withstand the conditions involved, it was found that the inner tubes of automobile tires were more suitable than any ordinary gasket material tried. Leather gaskets are completely destroyed. For holding the cover on the pressure bottle during heating an iron frame with a clamping device operated by a screw was used.

It was found expeditious to heat sealed tubes and pressure bottles submerged in water in an autoclave. By slowly heating and cooling the autoclave the difference in pressure on the inside and outside walls of the pressure bottle was never very great. By this expedient it was found practicable to use ordinary thin-walled 50 cc. Erlenmeyer flasks of pyrex glass as pressure bottles. They were successfully subjected to a temperature of 220°, which corresponds to a pressure of 330 pounds per square inch. In the matter of rubber gaskets, 180° to 190° is about the upper limit of temperature which can be employed without danger of rupture.

The usual procedure was to place the solution under investigation in a pressure bottle. After the pressure bottle (or sealed

tube) was closed it was placed in the autoclave, then during about two hours was slowly heated to the desired temperature. This temperature was maintained about six hours, after which about an hour was usually consumed in slowly reducing the temperature to 130°. Then the source of heat was removed and the autoclave allowed to cool overnight. On opening the bottles were uniformly found to have a negative pressure.

2. DECOMPOSITION OF BARIUM DITHIONATE

A. IN PRESENCE OF AIR. Fifty cubic centimeters of normal barium dithionate was placed in a pressure bottle of 380 cc. capacity and heated at 155° for an hour and a half. When the bottle was opened a white powder was observed, which weighed 2.6 grams after being collected on an alundum crucible. There was a strong odor of sulfur dioxide in the bottle. The white powder was thought to be barium sulfate, as would be inferred from the literature. An analysis of the powder in question yielded the following percentages of barium and sulfur.

	No. 1.	*No. 2.*	*Average.*	*Theor. % in $BaSO_4$*
Barium	56.511%	56.479%	56.495%	58.83%
Sulfur	14.180%	14.136%	14.158%	13.73%

From the foregoing it is evident that the solid formed in decomposing barium dithionate is too high in sulfur and too low in barium to be pure barium sulfate. Further a little computation shows that under the conditions of this experiment only about one third of the dissolved dithionate was decomposed.

It was next desired to ascertain the nature of the products of decomposition which, as above indicated, are not solely sulfate and sulfur dioxide. Consequently 2.67 grams of the solid residue, in nitric acid and bromine water, was digested overnight on a hot plate, the purpose being to dissolve any free sulfur, sulfites, thiosulfates, or other sulfur compounds convertible to sulfates or sulfuric acid by this method. The residue lost 6.8% of its weight in this process. The addition of barium chloride to the filtrate resulting from the digestion of the solid residue in nitric acid and bromine water yielded a precipitate of barium sulfate which weighed 0.1742 grams, or almost exactly the same as the weight lost by the original solid residue in the process of

digestion. As the difference between the molecular weights of barium sulfate and barium sulfite is only sixteen parts in more than two hundred, it seems a fair assumption, under conditions obtaining, to think that this acid-soluble portion of the original solid residue was chiefly barium sulfite.

The next objective attempted was to ascertain the final apportionment of sulfur among the end products of decomposition. If complete decomposition occurred, some insight into its nature should be obtained by learning how the entire quantity of sulfur in the original sample is apportioned among the various end products of decomposition.

The quantitative results from this series of experiments are recorded in the next succeeding table.

The attempt at complete recovery of sulfur among the end products involved the analysis of the liquid and gaseous contents of the pressure bottle after heating, as well as the analysis of the solid portion just described. It was not found necessary to determine barium dithionate among decomposition products. Sulfur dioxide, being present both as a gas and in solution, was determined by attaching the pressure bottle to an absorption system containing bromine water. The major part of the sulfur dioxide was driven over into the absorption system by heating the pressure bottle to a boiling temperature for one minute. Last traces of sulfur dioxide were swept from the pressure bottle by passing hydrogen through the system. The sulfur dioxide, after oxidation to sulfuric acid by the bromine water, was recovered as bromine sulfate by ordinary methods.

The procedure just recited served to remove the sulfur dioxide from the pressure bottle, and served to tell how much of the original sulfur was thus accounted for. There remained the solid and liquid portions in the pressure bottle. The solid portion was recovered on an alundum crucible and treated as already mentioned. The liquid portion was titrated with standard alkali and phenolphthalein. This titration showed a rather high acidity in the solution. Further, the addition of barium chloride in the presence of a slight excess of hydrochloric acid and subsequent recovery of the barium sulfate formed, showed that the alkali titration and weight of barium sulfate recovered harmonize with the assumption that sulfuric acid is the only sulfur compound present in the solution.

Summarizing findings to this point, it may be stated that under the conditions of the experiment the end products of decomposition of barium dithionate are barium sulfate, barium sulfite, sulfuric acid, and sulfur dioxide. In decomposition at 180° the quantity of sulfur dioxide found as an end product is negligible. The figures in the table represent percentages of sulfur on the original weight of barium dithionate taken as the sample. Barium dithionate contains 19.232% sulfur. Hence it is intended that on reading the figures "9.33, 9.62, 9.37, etc." down the column headed "% S as $BaSO_4$" the reader should understand that the weight of sulfur found in the end product barium sulfate in the different determinations corresponds to 9.33%, 9.62%, etc. of the weights of the respective original samples. Knowing that barium dithionate is 19.232% sulfur it might be correctly inferred that approximately half the sulfur in the original barium dithionate had been decomposed into barium sulfate. This same mode of setting forth results is employed throughout the paper.

TABLE NO. 1. DISTRIBUTION OF SULFUR AMONG END PRODUCTS EXPRESSED AS PERCENTAGE OF WEIGHT OF ORIGINAL SAMPLE DITHIONATE TAKEN.

Length of of time of decomposition	*% Total BaS_2O_6 decomposed*	*% S as $BaSO_4$*	*% S as $BaSO_3$*	*% S as SO_2*	*% S as H_2SO_4*	*% BaS_2O_6 in original solution*	*% of Total S recovered*
150° C. = Temperature at which decomposition occurred.							
1½ hr.	44.60	.....	.....	.....	.....	16.67	.....
1½	59.50	.....	.....	.....	.....	16.67	.....
6	99.12	9.33	0.31	5.95	3.06	4.00	97.00
6	98.43	9.62	0.16	3.01	5.10	4.00	93.20
180° = Temperature at which decomposition occurred.							
6	100.00	9.37	0.26	0.14	9.13	4.00	98.38
6	100.00	9.35	0.29	0.85	7.07	4.00	91.30
6	100.08	9.40	0.26	0.69	7.70	4.00	90.58

Observations on Foregoing Data.

1. The constancy of percentage of sulfur recovered as barium sulfate is notable. It is slightly less than half the sulfur originally in the barium dithionate. If to the percentages of sulfur in barium sulfate are added the percentages in the barium sulfite column the result, within the limits of experimental error, is exactly half the sulfur in the original sample.

2. The elimination of sulfur dioxide as a significant factor at the higher temperatures employed and the corresponding increase in the quantity of sulfuric acid formed is worthy of note.

3. The equation $2BaS_2O_6.2H_2O + O_2 = 2BaSO_4 + 2H_2SO_4 + 2H_2O$ fits the results of decomposition at 180° fairly well.

Thus, it appears that under the conditions of the experiment a four per cent solution of barium dithionate is decomposed into equimolecular quantities of barium sulfate and sulfuric acid. It is to be recalled that no effort was made to exclude air from the pressure bottle when the sample was being prepared for decomposition. As later developments show, this is a factor in tracing the course of the reaction.

B. Decomposition of Barium Dithionate in Absence of Air. It is pertinent to inquire as to the source of oxygen represented in the above equation. Measurement of the volume of air held in the pressure bottle during the time of decomposition showed there was present an excess of oxygen theoretically required by the equation for the quantities of dithionate decomposed. To learn if the oxygen of the air present in the pressure bottle was the source of the oxygen required by the above equation a second series of experiments, similar to the first, was performed, with these differences. The container was very much smaller and the air contained therein was replaced with nitrogen.

The stage in the experimental work immediately following was beset with some trouble from breaking and soluble pressure bottles along with non-concordant results. The work did not harmonize with previous experience. The chief reason for this, after elimination of poor pressure bottles, was found to arise from the fact that the exclusion of air introduced an entirely new factor as one of the end products, *viz.*, free sulfur. For some time its presence was not suspected. After it was known to be present some difficulty in the matter of separation and estimation was encountered, as ordinary methods of oxidation to sulfuric acid gave only partial oxidation after prolonged digestion. The entire recital of experiences encountered in the course of discovering the presence of free sulfur and the evolution of the methodology for its separation and estimation need not be recounted here, except in a very sketchy way. The presence of free sulfur was first established by noticing a flake of dark

colored substance in the solid residue collected on the alundum crucible. When this flake was placed on a foil and heated it manifested the properties of melting and burning sulfur. The earlier attempts at recovering free sulfur by oxidation methods failing, resort was had to ignition of the solid residue and estimation of free sulfur by difference. The sulfuric acid present was estimated as already indicated. By taking the values of sulfur thus obtained for barium sulfate, sulfuric acid, and free sulfur and ignoring small quantities of barium sulfite and sulfur dioxide the equation

$$3BaS_2O_6.2H_2O = 3BaSO_4 + 2H_2SO_4 + S + 4H_2O$$

fits the facts fairly well. A comparison of the percentages of sulfur theoretically required by the various members of this equation, with the corresponding percentages experimentally obtained, reveals the following. Each quantity represents a percentage of sulfur on the original weight of the dithionate sample.

	$3BaS_2O_6.2H_2O$	$= 3BaSO_4$	$+ 2H_2SO_4$	$+ S$	$+ 4H_2O.$
Theoretical	19.23	9.60	6.40	3.2	
Experimental	.....	8.32	6.60	2.2	

If the sulfite sulfur is added to the sulfate sulfur the showing is still better. These first results, while not overly reliable, because they show a rather singular 3:2:1 relation among the quantities of sulfur found in the products on the right side of the above equation are retained. Further they harmonize fairly well with later results.

Confirmation of Foregoing Results. All attempts at oxidation of free sulfur found in the solid residue gave non-concordant results. Indeed the oxidation of sulfur seldom advanced beyond the stage where small pieces of free sulfur were not visible to the eye. The method finally employed was to extract the free sulfur from the solid residue with acetone and weigh the extract as free sulfur, according to the method described for the determination of free sulfur in rubber by *Circular* 38, of the U. S. Bureau of Standards.

The chief desideratum sought in the following series of experiments was to learn whether or not the decomposition of barium dithionate in the absence of air gives the three chief products barium sulfate, sulfuric acid and free sulfur in the quantitative

relation represented in the last mentioned equation. The relatively small quantities of barium sufite and sulfur dioxide were temporarily ignored.

The pressure bottle used during decomposition was a 60-cc. Erlenmeyer flask of pyrex glass. In each instance a 4% solution of the dithionate in the presence of nitrogen was heated at 180° for six hours. After removal from the autoclave concentrated hydrochloric acid was added to the contents of the pressure bottle to insure the solution of any barium sulfite which might be present. The solid residue, consisting of barium sulfate and free sulfur, was next collected, washed and dried on an alundum crucible. After this the free sulfur was separated from the barium sulfate by extraction with acetone. The sulfuric acid formed by the decomposition of the dithionate was found in the filtrate arising from the collection of the original solid residue on the alundum crucible. The quantity of sulfuric acid present was determined in the usual manner by precipitation with barium chloride.

The figures in Table 3 represent percentages of sulfur on the weight of the original sample as in the preceding tables. Since barium dithionate contains 19.232% sulfur if decomposition into barium sulfate, sulfuric acid, and free sulfur represents the true facts of decomposition, the sum of their percentage sulfur in any given analysis should total 19.23%. It does this only approximately.

TABLE NO. 3. FINAL SHOWING OF DISTRIBUTION OF SULFUR AMONG END PRODUCTS AFTER DECOMPOSITION IN ABSENCE OF AIR.

180° = Temp. of Decomposition. 6 hrs. = Duration of heating.

% S Recov. as $BaSO_4$	*% S Recov. as H_2SO_4*	*% S Recov. as free S*	*% Total S Recovered*
8.47	7.25	*3.51	.....
8.98	8.42	*1.83	.....
8.60	6.65	2.32	91.8
7.99	7.41	3.40	97.7
8.49	8.43	2.85	102.5
8.64	7.91	2.80	100.0
8.58	8.18	2.30	99.3
8.53	7.73	2.72	98.2
% Theoret. required by eqn. $3BaS_2O_6.2H_2O = 3BaSO_4 + 2H_2SO_4 + S + 4H_2O$.			
9.61	6.41	3.20	.....

* Figures thus marked were obtained by difference.

Observations on results obtained in the foregoing table

1. There is a notable constancy in barium sulfate obtained.

2. The variations in results obtained for sulfuric acid and free sulfur are too large to be considered as checking in fair analytical work.

3. The results do not satisfactorily fit the hypothetical equation that has been set up.

4. Small but weighable quantities of barium sulfite have been ignored.

5. Sulfur dioxide also was ignored; yet on opening the pressure bottle after heating in the autoclave, in some of the above determinations a slight but appreciable odor of sulfur dioxide was observed. In others none was perceptible.

In view of the foregoing observations and other variations in the products of decomposition previously encountered, it was thought that the equations thus far proposed were untenable. In attempting to formulate a theory of decomposition harmonizing with observed experimental facts it would appear probable that the reaction does not proceed in one stage. The following assumptions seemed promising as a possible basis for the explanation of observed facts.

Assumption 1. In all cases the primary action is represented by the equation $BaS_2O_6.2H_2O = BaSO_4 + SO_2 + 2H_2O$.

Assumption 2. Barium sulfite is formed by double decomposition between undecomposed barium dithionate and sulfurous acid.

Assumption 3. Under the conditions of experiment the reaction represented by the equation $3H_2SO_3 = 2H_2SO_4 + S + H_2O$ proceeds to an appreciable extent. Rising temperature would displace this reaction to the right in accordance with the principle of LeChatelier.

These assumptions, if true, account for all the vagaries observed and indeterminate results obtained. Are these assumptions true?

Assumption 1 seems reasonable on its face beside being in harmony with the findings of other investigators.

Assumption 2 seems possible and probable. Only assumption 3 appears a bit unusual and perhaps doubtful. However, Jungfleisch and Brunell[30] found that this reaction proceeds at all

temperatures between 15° and 160°, while Lunge[31] further states that in the presence of sufficient oxygen, sulfate is the sole product.

Assumption 3 was experimentally verified for conditions most frequently used in the present work (180°) by sealing in a glass tube, of approximately 30 cc. capacity, 10 cc. of water saturated with sulfur dioxide. Previous to sealing, the air in the tube was replaced with gaseous sulfur dioxide. After sealing, the tube and contents were heated in the autoclave at 180° for six hours. On opening the tube globules of free sulfur were plainly visible and were found to weigh 0.0543 grams. In addition there were observed copious quantities of sulfur dioxide along with decisive quantities of sulfuric acid. The sulfur dioxide and sulfuric acid were determined only qualitatively. From the experimental results just mentioned and from the findings of Jungfleisch and Brunell it would seem that assumption 3 is tenable. The objection might be raised that there is no assurance that the actions mentioned in assumptions 1 and 3 will proceed simultaneously in the same vessel without materially modifying one or both reactions.

In order to see if the barium sulfate would modify the reaction $3H_2SO_3 = 2H_2SO_4 + S + H_2O$, the following experiment was performed. 0.5055 grams of barium sulfate suspended in 10 cc. of water was placed in a 60-cc. pressure bottle. The air in the pressure bottle was replaced with sulfur dioxide, the bottle closed and heated at 180° for six hours. The nature of the contents of the pressure bottle after being heated is shown by the following statement of materials recovered. Total solids recovered = 0.5261 grams; the weight of sulfur recovered from sulfur dioxide = 0.1082 grams; the weight of sulfur recovered from sulfuric acid = 0.1020 grams. The free sulfur recovered weighed 0.0092 grams. Also it is to be mentioned that the solid residue lost 0.0030 grams on hydrochloric acid digestion. In view of the very minute quantity involved it is doubtful if this last figure has any significance. So in a qualitative way it would appear that the presence of barium sulfate does not in any way interfere with the decomposition of sulfurous acid into sulfuric acid and free sulfur.

If the assumptions are true, the decomposition of barium dithionate as measured by the quantity of solid barium sulfate formed should be a monomolecular reaction. Some effort was

made to measure the speed of decomposition of barium dithionate, but without success. It was attempted to carry on the action with a series of samples in sealed tubes. Supposedly by subjecting them all to the same conditions of heating, a uniform condition of decomposition would be obtained. Then by successively removing one tube at a time, after various intervals, and analyzing its contents it should have been possible to arrive at the amount and rate of decomposition. This was not realized in practice. Very little consistent relation was observed between the temperature, time of heating, and resulting degree of decomposition. Apparently, as already mentioned under the preparation of dithionates, there is a factor or factors involved in decomposition that has not been discovered.

In connection with the matter of decomposition is to be mentioned the work of Muller[24] who studied the reaction

$$Na_2S_2O_6 + I_2 + 2\ H_2O = 2\ NaHSO_4 + 2\ HI,$$

and found it to be monomolecular. This led Muller to think the action proceeded in three steps, viz.: (1) Liberation of dithionic acid, (2) its decomposition into sulfurous and sulfuric acids and (3) the action of iodine on sulfurous acid. The time for 1 and 3 is negligible compared with 2, so that 2 only is measured. He found that the velocity constant at 51.3° was 0.00836 and that velocity increased with rising temperature.

C. Modifying Factors

The purpose of these experiments was to see if the decomposition of barium dithionate was influenced by the presence of any of the products of decomposition that were likely to be present. In each instance the plan pursued was to place one gram of barium dithionate contained in 10% solution in a pressure bottle. The pressure bottle and contents were heated in the autoclave for one hour at 120°. This produced only partial decomposition. By weighing the quantity of barium sulfate formed, the extent to which decomposition had proceeded was ascertained. After it was learned to what extent decomposition had proceeded under these conditions, the effect produced on decomposition by the addition of small quantities of various substances to the solution during heating was studied. The procedure was the same as that employed for the pure barium dithionate solution already outlined, except that small quantities of sodium thiosulfate,

barium sulfate, sulfur dioxide and free sulfur were successively added to the contents of the pressure bottle before it was placed in the autoclave.

TABLE 4. SHOWING THE WEIGHTS OF BARIUM SULFATE OBTAINED BY HEATING 10 CC. OF A 10% SOLUTION OF BARIUM DITHIONATE FOR ONE HOUR AT 120° ALONE AND WITH THE ADDITION OF SMALL QUANTITIES OF A THIOSULFATE, A SULFATE, SULFUR DIOXIDE, AND FREE SULFUR.

Initial substance in pressure bottle during heating.	*Weight of barium sulfate obtained after heating.*		
	No 1.	No. 2.	No. 3.
Nothing but BaS_2O_6	0.1331	0.2651	0.1953
BaS_2O_6 + free sulfur	0.1180	0.1970	.....
$BaS_2O_6 + BaSO_4$	0.2614	0.4395	0.3591
$BaS_2O_6 + SO_2$	0.6260	0.6414	0.6320
$BaS_2O_6 + Na_2S_2O_3$ Initial action was precipitation of BaS_2O_3.			

About all that can be said of the foregoing results is that sulfur dioxide accelerates the decomposition of barium dithionate. It would seem probable that the first action was the formation of dithionic acid and sodium sulfite by double decomposition and that dithionic acid decomposes more readily than the salts examined in this investigation. With the idea that sulfur dioxide accelerates the decomposition of barium dithionate the next experiment was performed to see if this effect was observable at room temperature. Sulfur dioxide was bubbled through 10 cc. of a 10% solution of barium dithionate during four hours at room temperature, causing appreciable decomposition; 0.0687 grams of solid was obtained. No analysis was attempted.

Sulfur dioxide was bubbled through a 10% barium dithionate solution as before, resulting in the formation of a solid white powder, but on continued passage of sulfur dioxide the solid formed redissolved. On attempting to learn the composition of the white precipitate thus formed, manipulation with a solution containing 30 grams of barium dithionate failed to yield enough solid with which to work. As a first surmise it might be thought that the solid thus formed was barium sulfate; but, as in a further experiment it was found that a suspension of barium sulfate lost no weight when treated with sulfur dioxide for twenty-four hours, the most probable hypothesis is that the first product formed is barium sulfite, which on continued passage of sulfur dioxide is converted to soluble barium acid sulfite.

The point in the foregoing arises from the fact that if the solid thus formed is barium sulfite it may offer corroborative evidence as to the truth of the second assumption.

After the study of the decomposition of the dithionic salts of some other metals the probable truth of the three assumptions in the light of experimental data adduced will receive further discussion.

3. THE DECOMPOSITION OF SOME OTHER DITHIONATES

The other dithionic salts studied were those of potassium, cadmium, and nickel. The first and third assumptions set up to account for the decomposition of barium dithionate were found applicable throughout. No sulfites of metals were detected in this latter part of the work. The decomposition of cadmium and nickel dithionates yielded small quantities of the respective sulfides. It is possible that sulfites were present in small quantity but escaped detection. The weight of the free sulfur and sulfide combined for the cadmium and nickel salts weighed from ten to twenty milligrams.

A. Potassium Dithionate

Free sulfur was the only insoluble product of decomposition. A five percent solution was heated to 180° during six hours. No sulfite nor thiosulfate could be detected.

Table 5. Showing Distribution of Sulfur Among End Products After Decomposition of Potassium Dithionate in Absence of Oxygen.

Potassium dithionate = 26.91% Sulfur.

	% S as K_2SO_4	*% S as* H_2SO_4	*% as free S*	*% S as* SO_2	*Total % S Recovered*
No. 1	13.23	7.69	2.82	0.06	23.80
No. 2	12.84	9.56	2.62	0.44	25.46

The mode of analysis was along lines similar to those employed for barium dithionate decomposition.

B. Cadmium Dithionate

Abegg describes this salt as being efflorescent and having six molecules of water of crystallization. By an analysis for sulfur it was found that crystals of this salt dried by exposure to the air at room temperature were without water of crystallization.

A saturated solution of cadmium dithionate decomposes at 85°. In a pressure bottle a 10% solution was not completely nor even extensively decomposed after heating three hours at 125°.

In the analytical portion of this work, after decomposition had been effected, the solid products thus arising were collected on an alundum crucible and weighed, after which the cadmium sulfide was dissolved by hydrochloric acid, and the remaining sulfur weighed. The manipulation of liquid and gaseous products was similar to that already described for the decomposition products of barium dithionate.

TABLE 6. SHOWING DISTRIBUTION OF SULFUR AMONG END PRODUCTS ARISING FROM DECOMPOSITION OF CADMIUM DITHIONATE IN ABSENCE OF OXYGEN.

$CdS_2O_6 = 23.537\%$ sulfur. 5% — Concentration of solution used.

Temp. of Decomp.	*% S as $CdSO_4$*	*% S as H_2SO_4*	*% S as SO_2*	*% S as free S*	*% S as CdS*	*Total % S recovered*
150°	10.69	3.42	9.11	Test	Test	22.22
180°	12.94	7.53	1.05	0.19	Test	22.71
180°	13.05	7.61	0.00	2.41	0.28	23.35
200°	13.30	8.16	.....	.....	.....	21.46

C. NICKEL DITHIONATE

The nickel dithionate used was not crystallized from the solution in which it was formed. As the exact concentration of nickel dithionate solution suffering decomposition was not known the following figures represent the weights of sulfur found in the various products of decomposition.

DISTRIBUTION OF SULFUR AMONG PRODUCTS OF DECOMPOSITION
Decomposed at 180° for six hours.

$NiSO_4$	*H_2SO_4*	*NiS*	*Free S*	*SO_2*
0.0914 g.	0.1259 g.	0.0082 g.	0.0051 g.	0.0164 g.

The chief object in pursuing this phase of the work was to learn whether the products of decomposition of potassium, cadmium, and nickel dithionates were materially different in kind and quantity from those obtained by decomposition of barium dithionate. Apparently the state of aggregation of the end products or the potential formation of insoluble sulfides plays no role in the general course of the reaction in the various cases observed.

VI. DISCUSSION AND CONCLUSIONS

The following comprises a consideration of the foregoing experimental work and to some extent the work of others in relation to (1) the formation of dithionates and (2) the decomposition of dithionates.

1. THE FORMATION OF DITHIONATES

The survey of the literature already recounted shows that the course of the action or actions resulting in the formation of manganese dithionate and manganese sulfate, in variable proportions, by the action of sulfur dioxide on manganese dioxide has been the subject of considerable investigation and speculation. With most writers the crux of the question has been "Are the dithionate and sulfate formed consecutively or simultaneously?" That is, is the dithionate intermediate between the sulfite and sulfate?

To the present writer it seems that, probably, the actions are consecutive and that the dithionate is an intermediate product between the sulfite and the sulfate, that the primary action is that mentioned by Marino[26], $MnO_2 + 2SO_2 = MnS_2O_6$, and that the sulfate is formed by the decomposition of the manganese dithionate into manganese sulfate and sulfur dioxide. Supporting this view is the fact experimentally adduced that sulfur dioxide accelerates the decomposition of dithionates. Some doubt is cast upon the findings of Antony and Lucchesi[17] which conflict with the ideas just advanced by the internal evidence of their own work. These authors thought they had obtained ruthenium dithionate by the action of sulfur dioxide on ruthenium sulfate. Later they state that the ruthenium dithionate thus formed was decomposed by the action of potassium permanganate. Others have unsuccessfully attempted to decompose dithionates with permanganate. So in the absence of corroborative evidence the work of Antony and Lucchesi, in this connection, is to be accepted with reservation. The findings of J. Meyer[25], Carpenter[19], and Marino[26], already mentioned, may be interpreted by supposing that the manganese sulfate which these authors found occurring with manganese dithionate when sulfur dioxide and manganese dioxide are brought together is the result of decomposition of manganese dithionate into manganese sulfate and sulfur dioxide. The higher the tempera-

ture of the reactions the more the decomposition is promoted and consequently the more manganese sulfate there is formed. In view of the simplicity of this viewpoint as well as its harmony with experimental evidence it appears to be a better theory than the inductor theory, though it is quite possible that both theories are correct.

Summarizing this part of the study it may be said, in view of the findings of others and the present experimental results, that the following conclusions may be fairly drawn concerning the formation of manganese dithionate and manganese sulfate simultaneously by the action of sulfur dioxide on manganese dioxide in water suspension.

A. Conclusions on Formation

1. The first action, as suggested by Marino[26], is that represented by the equation

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

2. Simultaneously a portion of the manganese dithionate decomposes into manganese sulfate and sulfur dioxide.

3. The variation in the proportion between the quantities of sulfate and dithionate formed is to be accounted for by the effect of variation in temperature on the action mentioned in the second conclusion.

2. The Decomposition of Dithionates

It is believed that a perusal of the experimental part of this work demonstrates the following facts with respect to the spontaneous decomposition of dithionates in water solutions in closed systems at the temperatures mentioned.

1. The final products are chiefly metallic sulfates along with sulfur dioxide, sulfuric acid, and free sulfur in variable proportions. In addition are found minute quantities of sulfites and sulfides on decomposing the dithionates of metals capable of forming insoluble sulfites and sulfides.

2. When sufficient oxygen is present, sulfur is not found as an end product but is converted to sulfate.

3. Rising temperatures diminish the quantity of sulfur dioxide found as an end product and cause a corresponding increase in the sulfuric acid formed.

4. Sulfur dioxide accelerates the decomposition of dithionates.

5. Subjecting a mixture of a saturated solution of sulfur dioxide in water and gaseous sulfur dioxide to conditions of most of the experimental work results in the formation of appreciable quantities of sulfuric acid and free sulfur.

From these experimental facts the following conclusions seem warranted as explaining the mechanics of the decomposition of the dithionates studied. These conclusions are partly contained in the first and third assumptions mentioned in connection with the work on barium dithionate.

A. Conclusions Respecting Decomposition of Dithionates

1. In all cases the primary decomposition results in the formation of metallic sulfate and sulfur dioxide.

2. All other products experimentally obtained arise from the subsequent action or interaction of the three substances, undecomposed dithionate, sulfur dioxide, and metallic sulfate.

Under conclusion 2 and arising from considerations there mentioned may be appended the following corollaries.

Cor. 1. The action represented by the equation

$$3\ SO_2 = 2SO_3 + S$$

under the conditions of this work proceeds sufficiently to account for the free sulfuric acid and free sulfur found as end products.

Cor. 2. The sulfites found were formed by double decomposition between undecomposed dithionate and sulfurous acid.

Cor. 3. Sulfides found were formed by direct union between nascent sulfur arising from the action mentioned in corollary 1 and the ions of the metal in question.

Just why sulfites and sulfides mentioned in corollaries 2 and 3 should exist in the presence of sulfuric acid of concentrations found is not apparent. However, that unusual conditions of temperature and pressure as well as the presence of extraneous substances sometimes greatly modify solubilities is well known.

The following results, not obtained experimentally, might be expected to arise from the operation of well known chemical principles in the decomposition of dithionates under the conditions observed.

1. Thiosulfates should arise from heating sulfites in the presence of free sulfur.

2. Sulfites should be formed to some extent in all cases of decomposition of dithionates, but for various causes are so modified as to escape detection.

It may be here observed that an action similar to that mentioned in corollary 1 should convert sulfites to sulfates and free sulfur.

In the matter of structure the author, at present, has no contribution to offer in addition to what is already afforded in the literature. That the present status is unsatisfactory is acknowledged but apparently not to be helped until a more intimate knowledge of atomic and molecular structure is forthcoming.

Concerning the phenomenon termed "autoxidation" spoken of in the earlier part of the paper, it may be mentioned that the decomposition of dithionates where one of the sulfur atoms in the dithionate molecule forms sulfate with a sulfur valence of six, while the other sulfur atom of the same dithionate molecule forms sulfur dioxide with a sulfur valence of four is a phenomenon of this kind. Here also is included the splitting of sulfur dioxide into sulfur trioxide and free sulfur. Here is an inviting and little explored field.

VII. ACKNOWLEDGMENTS

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VIII. REFERENCES TO THE LITERATURE

1. Welter and Gay-Lussac. Annales de chimie et de physique. 10, 312. 1819.
2. Langlois. Annales de chimie et de physique. (iii) 4, 77. 1842.
3. Fordos and Gelis. Annales de chimie et de physique. (iii) 6, 484. 1843.
4. Wackenroder. Archiv der Pharm. 97, 272. 1845.
5. Debus. Journal of the Chemical Society. 53, 278. 1888.
6. Fordos and Gelis. Annales de chimie et de physique. (iii) 22, 66. 1848.
7. Thomsen, Thermochemische Untersuchungen. 1882. II, p. 259 *et. seq.*

8. Heeren. Annalen der Physik und Chemie. Poggendorff. 7, 55 also 171. 1826.
9. Jacquelain. Annales de chimie et de physique. (iii) 21, 110. 1847.
10. Pean de Saint Gilles. Annales de chimie et de physique. (ii) 55, 374.
11. Hauer. Journal für praktische Chemie. 80, 229. 1860.
12. Gelis. Annales de chimie et de physique. (iii) 65, 222. 1862.
13. Rathke and Zschiesche. Journal für praktische Chemie. 92, 141. 1864.
14. Sokolow and Multschewski. Journal of the Russian Physical Chemical Society. 1, 169. 1881.
15. Kluss. Annalen der Chemie. Liebig's. 246, 179. 1888.
16. Berthelot. Comptes rendus. 108, 773. 1889.
17. Antony and Lucchesi. Gazetta chimica italiana. 28, (II) 139.
18. Nabl. Monatshefte für Chemie. 22, 737. 1901.
19. Carpenter. Journal of the Chemical Society. 81 (I) 1. 1902.
20. Foerster and Friessner. Berichte der deutschen chemischen Gesellschaft. 35, 2515. 1902.
21. Friessner. Zeitschrift für Elektrochemie. 10, 265. 1904.
22. Baubigny. Annales de chimie et de physique. 20, 5. 1911.
23. Baubigny. Annales de chimie. 1, 201. 1914.
24. Muller. Bulletin de la societe chimique de France. (iv) 9, 183. 1911.
25. J. Meyer. Berichte der deutschen chemischen Gesellschaft. 34, 3606. 1901.
26. Marino. Gazetta chimica italiana. 38, (I) 249. 1908.
27. Abegg's "Handbuch". Vol. 4, Part 2, page 731.
28. Luther and Schilow. Zeitschrift für physikalische chemie. 46, 777. 1903.
29. Schilow. Zeitschrift für physikalische chemie. 42, 641. 1903.
30. Jungfleisch and Brunell. Comptes rendus. 156, 1719. 1913.
31. Lunge. Sulfuric Acid and Alkali. 1908. Vol. I, Part 1, page 151.

AUTOBIOGRAPHY

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